

GRAFTING OF HYDROXY-TERMINATED POLYBUTADIENE WITH 2-MERCAPTOETHANOL

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A method for functionalization of hydroxy-terminated polybutadiene with 2-sulfanylethan-1-ol (2-mercaptopropanoic acid) leading to a controlled increase in the OH functionality of the polymer was developed. The polybutadiene used contained about 65% of unsaturation in the form of 1,2-vinyl groups. The reaction was carried out without using volatile solvents. The radical addition of 2-sulfanylethan-1-ol on the polymer proceeded quantitatively and the products were free of the mercaptan odour. A series of functionalized polybutadienes were synthesized and characterized by their physical and chemical properties. The differential scanning calorimetry and thermogravimetric analysis measurements revealed that the functionalization improves the stability of the polybutadiene to thermooxidation. The obtained polymers were used for the preparation of polyurethane elastomers. The effect of the increased functionality of the polybutadiene on mechanical properties, thermal behavior and hydrolytic resistance of the elastomers was assessed.

Keywords: Hydroxy-terminated polybutadiene; 2-Sulfanylethan-1-ol; Radical addition; Functionality; Thermooxidation stability; Polyurethane elastomers; Functionalized polymers.

Liquid hydroxy-terminated polybutadienes (HTPB) are used as components in the production of special polyurethanes exhibiting excellent hydrophobicity, hydrolytic resistance, electrical insulation properties and low-temperature elasticity¹⁻³. HTPB products provide a unique set of properties advantageous in a wide range of applications such as polyurethane elastomers, sealants, adhesives, coatings and binders^{4,5}.

Commercial polybutadiene diols Krasol LBH manufactured by Kaučuk, a.s. (Czech Republic) are prepared by a process involving anionic polymerization of butadiene followed by the reaction of "living" chain ends with propylene oxide. Liquid polybutadienes Krasol LBH are well-defined linear polymers⁶ terminated mostly by secondary hydroxy groups of 2-hydroxypropyl units. They contain no species with functionality higher than 2. While for most applications this unique feature is advantageous, the use of

such polymers in polyurethane systems requiring chemically crosslinked network may be limited.

Regarding the microstructure of Krasol products, approximately 65% of butadiene structure units in the polymer chain are vinylethylene units⁷. This characteristic affects the viscosity of liquid polybutadiene, its glass transition temperature, thermooxidation stability, resistance to UV radiation and other properties.

The objective of the work was to increase the hydroxy functionality of Krasol LBH by a polymer modification reaction. A grafting of HTPB with a sulfanyl alcohol appears a promising way, since the addition of mercaptans on polydienes has already been used for the introduction of various functional groups into the polymer chain⁸⁻¹¹.

A recent paper of Boutevin *et al.*¹² reports on the functionalization of HTPB with 2-sulfanylethan-1-ol initiated with 2,2'-azobis(isobutyronitrile). The HTPB products used in this study were radical-polymerized polybutadienes PolyBd R45HT and PolyBd 20LM. The reaction was performed in solution as well as in bulk. In all cases, the addition of 2-sulfanylethan-1-ol was not complete, which is not acceptable for industrial applications¹².

The published data suggest that the addition of thiol groups on the polybutadiene chain proceeds preferentially on vinyl double bonds^{11,12}. Since the content of vinyl double bonds in Krasol polybutadienes is much higher than in PolyBd products (*ca* 65 vs 20%), we considered it useful to functionalize the Krasol polymer with 2-sulfanylethan-1-ol. The functionalization was performed in bulk to allow an industrial scale-up. The obtained HTPB polymers were tested as components for polyurethane elastomers.

EXPERIMENTAL

Materials

Two commercially available HTPB products were used. Krasol LBH 2000 is a product of Kaučuk, a.s. (Czech Republic). The polybutadiene was stabilized by *ca* 0.15% of a phenolic antioxidant (Irganox 1520, Ciba). PolyBd R45HT was obtained from the Elf Atochem Co. (France). Their characteristics are given in the Table I.

Krasol NN-22, an isocyanate prepolymer based on liquid polybutadiene and diisocyanato-diphenylmethane (MDI), was also a product of Kaučuk, a.s. The characteristics of Krasol NN-22 were as follows: NCO content 2.11 mmol/g, Brookfield viscosity 12 800 mPa s at 25 °C.

2-Sulfanylethan-1-ol (2-mercptoethanol, Fluka), 2,2'-azobis(isobutyronitrile) (AIBN, Elf Atochem) and dibutyltin dilaurate (Crompton-Witco) were used as received. 2-Ethylhexane-1,3-diol (Aldrich) was dried under vacuum until the content of water was below 0.03 wt.%.

TABLE I

Synthesis and characterization of hydroxy-terminated polybutadienes (HTPB) functionalized with 2-sulfanylethan-1-ol

Parameter	LBH X02	LBH X05	LBH X10	LBH X20	LBH 2000 ^a	PolyBd ^b
Synthesis						
Krasol LBH 2000 (g)	800	800	800	800	—	—
2-Sulfanylethan-1-ol (g)	7.05	14.10	28.19	56.39	—	—
2,2'-Azobisisobutyronitrile (g)	0.64	0.64	0.64	0.64	—	—
Theoretical values ^c						
OH content (mmol/g)	0.969	1.072	1.271	1.651	—	—
Bound sulfur (%)	0.36	0.71	1.40	2.70	—	—
Properties						
OH content (mmol/g)	0.968	1.085	1.275	1.625	0.865	1.047; 0.85 ^d
M_n	2210	2200	2230	2320	2090	2950; 2700 ^d
M_w/M_n	1.26	1.26	1.25	1.25	1.23	2.47; 2.50 ^d
Glass transition temperature (°C)	-39	-38	-36	-31	-41	-78
Viscosity Brookfield (mPa s)						
25 °C	16000	19200	27900	58400	13400	7380
30 °C	9810	11800	16600	33600	8240	5520
40 °C	4050	4750	6580	12400	3480	3190
50 °C	1930	2250	3000	5430	1670	1960
60 °C	1050	1180	1560	2660	902	1310
70 °C	643	696	845	1420	538	902
80 °C	403	432	509	806	341	662

^a Krasol LBH 2000; ^b PolyBd R45HT; ^c calculated from stoichiometry; ^d data given by the producer.

Synthesis

Reaction of 2-Sulfanylethan-1-ol with HTPB

The reaction was carried out in a heated 1.5-l sulfonation flask with an agitator, nitrogen inlet and openings for charging the components. Krasol LBH 2000 was heated to 90 °C and bubbled through with nitrogen to remove traces of oxygen if present in the polymer. 2-Sulfanylethan-1-ol (10–100 mmol/100 g polybutadiene) containing the first portion of AIBN (0.24 mmol/100 g polybutadiene) was added and the mixture left to react at 90 °C. After 1-h reaction, the second portion of AIBN (0.24 mmol/100 g polybutadiene) was charged. The total reaction time at 90 °C was 2 h. At the end of the synthesis the product was heated at 130 °C for 1 h to decompose the unreacted AIBN. The reaction temperature and dosage of AIBN were not optimized.

Preparation of Polyurethane Elastomers

The components of the polyurethane mixture were charged into a 350-ml glass bottle in the following order: HTPB, 2-ethylhexane-1,3-diol, Krasol NN-22 and dibutyltin dilaurate. After each addition the content was thoroughly mixed and degassed under vacuum. The final blend was immediately poured into polypropylene molds and cured at laboratory temperature for 20 h. After demolding, the samples were conditioned at laboratory temperature for at least four weeks prior to testing.

The dose of dibutyltin dilaurate in the formulations was set to give the pot-life 90–120 min. The pot-life was determined by measuring the course of viscosity of the blend as the time needed to reach the Brookfield viscosity of 1600 Pa s.

Methods

Number- and weight-average molecular weights M_n and M_w of the polymers were determined by gel permeation chromatography (GPC). A Waters GPC (Milford, MA, U.S.A.) equipped with a refractive index detector 410 and a diode-array detector (DAD) 996 was employed for the measurement. Two temperature-controlled (30 °C) ultraStyragel columns of nominal pores 10^3 and 10^4 Å were used. The mobile phase was tetrahydrofuran at a flow-rate of 1 ml/min. All samples were dissolved in tetrahydrofuran (0.15% w/v) and toluene was added as an internal standard to correct for variations in the carrier flow-rate. The injection volume was 100 µl. For the molecular weight calibration, authentic standards were not available. For this reason, a universal calibration was used. Polystyrene standards with narrow-molecular-weight distribution from Polymer Laboratories (Shropshire, U.K.) were employed for calibration. Mark–Houwink coefficients for polystyrene ($a = 0.713$, $K = 1.25 \times 10^4$ dl/g) and polybutadiene with 70% content of 1,2-structures ($a = 0.693$, $K = 4.03 \times 10^{-4}$ dl/g) were taken from the Polymer Handbook. The data were collected and treated by chromatographic software Millenium.

Determination of hydroxy groups was performed by acetylation with acetic anhydride and pyridine according to ASTM E 222 A.

Viscosity was measured on a Brookfield viscometer, model DV-II+ using a small sample adapter.

2-Sulfanylethan-1-ol in polybutadiene was determined by gas chromatography after dissolving the sample in ethyl acetate using a Hewlett-Packard 5890 series II gas chromatograph with FID, equipped with a fused silica capillary column DB-1 (J&W Scientific) of 15 m

length, 0.53 mm i.d. and 1.5 μm film thickness. The carrier gas was nitrogen of 7 ml/min flow rate, the temperature was 60, 200 and 250 $^{\circ}\text{C}$ in oven, injection head and detector, respectively. Quantitative data were calculated using nonane as an internal standard. The column was conditioned at 230 $^{\circ}\text{C}$ after each run.

Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature (T_g) of the polymers. The measurements were performed on a DSC 2010 apparatus (TA Instruments) under nitrogen. The samples were cooled to -80 $^{\circ}\text{C}$ (or -140 $^{\circ}\text{C}$ in the case of PolyBd R45HT) and the first scan was made at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ up to 20 $^{\circ}\text{C}$. Then, the samples were again quenched to the required temperature and left there for 5 min before the second scan at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ gave the values of T_g , taken at the inflection point of the heat capacity jump of the glass transition.

DSC measurements on the same apparatus were used to study the thermooxidative stability of the polymers. The DSC curves were recorded in the temperature interval from 50 to 300 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ using open aluminium pans in air (40 ml/min). The sample size was 4 mg.

Thermogravimetric analysis (TGA) was carried out on a TA Instruments analyzer Q 500 in air atmosphere. The samples were heated from ambient temperature at a uniform rate of 5 $^{\circ}\text{C}/\text{min}$. The sample weight was about 10 mg.

Properties of the polyurethanes prepared from HTPB products were measured by the following standard methods: Shore hardness (ISO 868:1997), tensile stress-strain properties (ISO 37:1994, modified: stress-strain properties of a specimen with maximum tensile strength are given as results) and compression set (ISO 815:1991).

The glass transition temperature (T_g) and the softening temperature (T_m) of the polyurethanes were measured by dilatometry using a thermomechanical analyzer TMA-CX04R (Intertec Ltd., Czech Republic).

The hydrolysis resistance of polyurethane elastomers was studied in steam at 100 $^{\circ}\text{C}$ using 130 \times 65 \times 2 mm elastomer sheets. After 28-day exposure the weight change of the elastomer was determined. Then specimens for tensile testing were die-stamped from these sheets.

RESULTS AND DISCUSSION

Functionalization Reaction

The functionalization reaction of 2-sulfanylethan-1-ol on hydroxy-terminated polybutadiene Krasol LBH 2000 was performed without volatile organic solvents. The addition was initiated with a radical initiator, 2,2'-azobis(isobutyronitrile). The initiator was charged into the reaction mixture in two portions, in the beginning and after 1 h, to ensure its availability during the whole reaction period. The amounts of 2-sulfanylethan-1-ol per polybutadiene were approximately 0.25, 0.5, 1.0 and 2.0 mol per mol, yielding functionalized HTPB designated LBH X02, LBH X05, LBH X10 and LBH X20.

In all cases, the reaction started immediately after mixing 2-sulfanylethan-1-ol containing the first portion of AIBN with the preheated Krasol

LBH 2000. The onset of the reaction was indicated by a remarkable increase in temperature of the reaction mixture.

In the course of the synthesis, the content of free 2-sulfanylethan-1-ol in the product was monitored by analyzing the samples withdrawn from the reactor by gas chromatography. For all the syntheses, the 2-h reaction time was sufficient to reach virtually total conversion, *i.e.* the content of 2-sulfanylethan-1-ol was below the detection limit of the method (0.001%). The functionalized polymers are free of the mercaptan odour. It was verified that the presence of the antioxidant in Krasol LBH 2000 did not interfere with the functionalization.

The preparation conditions and characteristics of the HTPB products are summarized in Table I. Properties of the starting polybutadiene Krasol LBH 2000 and of PolyBd R45HT are also presented for comparison. It should be noted that some of the data for PolyBd R45HT obtained by us significantly differed from those given by the producer.

The content of OH groups in the functionalized polymers increased in dependence on the amount of added 2-sulfanylethan-1-ol. The found OH contents were very close to the theoretical ones. The reaction with 2-sulfanylethan-1-ol led to a small increase in molecular weight of the polymers, the changes in polydispersity were not significant. The glass transition temperatures of the polymers increased proportionally with the thiol content.

At room temperature, Krasol LBH 2000 is more viscous than PolyBd R45HT, while at higher temperatures the viscosity of Krasol is lower than that of PolyBd. This effect can be attributed to different microstructure of the polymers. The viscosity of the functionalized polymers is affected by the amount of added 2-sulfanylethan-1-ol. After the reaction, the polymers exhibited remarkably higher viscosity at room temperature. The viscosity of the functionalized polymers drops with increasing temperature more rapidly than in the case of unmodified Krasol LBH 2000, which suggests an association of hydroxy groups.

The results in Table I show that the content of hydroxy groups introduced into polybutadiene by functionalization with 2-sulfanylethan-1-ol can be simply controlled by stoichiometry. The products obtained by functionalization of Krasol LBH 2000 bear two types of hydroxy groups: secondary OH on chain ends from the starting polymer and primary OH groups coming from 2-sulfanylethan-1-ol.

We have proved that, using the same procedure, the functionalization can be carried out on polybutadiene with terminal primary OH groups (Krasol LBH-P) as well as on polybutadiene without functional groups

(Krasol LB), both with full conversion. In both the cases, the functionalized polymers contain solely primary OH groups. Furthermore, the feasibility of the synthesis on a large scale was verified in a 15-l stainless steel reactor (data not presented in this paper).

Polyurethane Elastomers

The products obtained by functionalization of hydroxy-terminated polybutadiene with 2-sulfanylethan-1-ol were used for preparation of polyurethane elastomers. For comparison, the elastomers were prepared also from unmodified Krasol LBH 2000 and PolyBd R45HT (Table II). Our objective was to determine the role of average functionality of HTPB for application in polyurethane systems.

The formulations consisted of HTPB, 2-ethylhexane-1,3-diol as a chain extender, polybutadiene MDI prepolymer (Krasol NN-22) as an isocyanate component, and dibutyltin dilaurate as a catalyst. The hard segments of the polyurethanes were formed by 2-ethylhexane-1,3-diol and MDI-type isocyanate contained in the Krasol NN-22 prepolymer. For all the formulations, the hard segment content was 21%, and the NCO/OH ratio was 1.00. It was observed that with increasing OH functionality of HTPB, the cross-linking reaction was faster. Thus, to achieve the same pot-life for all the formulations, the dosage of catalyst had to be lowered.

The elastomers were characterized by their mechanical properties, T_g and T_m . The hydrolytic and thermal stability of the elastomers was studied using steam at 100 °C as a medium.

The results in Table II demonstrate that the increasing average OH functionality of HTPB increased the Shore hardness, improved the compression-set characteristics and dramatically decreased elongation of the elastomers. We assume that the differences in characteristics of the elastomers are attributable to an increase in the crosslink density of polyurethane networks. Polybutadiene LBH X20 with the highest average functionality yielded an overcrosslinked crumble elastomer with high hardness and low elongation. The changes in tensile strength were not so remarkable.

The elastomer from unmodified Krasol LBH 2000 had rather low softening temperature and exhibited thermoplastic behavior in compression test. With increasing crosslink density, the stability of the elastomers on heating improved.

In the hydrolysis test, Krasol-LBH-2000-based material melted in steam on the first day. The elastomer from LBH X02 had somewhat higher thermal stability and retained shape during 14-day exposure to steam. The

TABLE II
Preparation and characterization of polyurethane elastomers

Parameter	LBH X02	LBH X05	LBH X10	LBH X20	LBH 2000 ^a	PolyBd ^b
Average functionality ^c	2.14	2.38	2.85	3.77	1.81	3.09; 2.4-2.6 ^d
Elastomer composition						
HTPB (g)	100.0	100.0	100.0	100.0	100.0	100.0
2-Ethylhexane-1,3-diol (g)	8.3	7.8	7.1	5.7	8.6	7.9
Krasol NN-22 (g)	99.7	102.0	106.0	114.0	98.3	102.0
Dibutyltin dilaurate (g)	0.0033	0.0022	0.0011	0.0000	0.0033	0.0025
Elastomer properties						
Hardness (Shore A)	48	54	58	65	43	53
Ultimate elongation (%)	470	310	210	110	870	260
Tensile strength (MPa)	5.9	5.9	4.5	3.7	6.8	4.1
100% modulus (MPa)	1.1	1.8	2.1	3.5	1.2	1.8
200% modulus (MPa)	1.7	3.1	4.2	-	1.6	3.1
300% modulus (MPa)	2.6	5.4	-	-	2.1	-
400% modulus (MPa)	4.1	-	-	-	2.7	-
500% modulus (MPa)	-	-	-	-	3.3	-
Compression set (%)						
25 °C, 72 h	38	18	7	7	73	19
70 °C, 24 h	60	33	22	14	106	48
Glass transition temperature, T _g (°C)	-35	-37	-35	-29	-38	-64
Softening temperature, T _m (°C)	125	162	185	208	97	160
Hydrolysis resistance ^e						
Weight, change (%)	-1.72 ^f	-0.46	-0.78	-0.69	n.t.	-0.64
Ultimate elongation, change (%)	n.t.	+325	+290	+315	n.t.	+64
Tensile strength, change (%)	n.t.	-11.4	+15.2	+33.6	n.t.	-15.6
100% modulus, change (%)	n.t.	-50.9	-59.0	-61.4	n.t.	-51.4

^a Krasol LBH 2000; ^b PolyBd R45HT; ^c calculated as: average functionality = OH content (mmol/g) × M_n (g/mol) × 0.001 (mol/mmol), where M_n is the number-average molar mass of the polymer, which is numerically equal to M_n (cf. Table I); ^d data given by the producer; ^e steam at 100 °C, 28 days; ^f measured after 14 days; n.t., not tested due to deformation of the sample.

HTPB-based elastomers with functionality higher than 2.3 exhibited good stability in the hydrolysis test. However, the evaluation of tensile properties after hydrolysis showed a significant increase in elongation and 50–60% drop in modulus. These data indicate partial degradation of the polyurethane network of the elastomers.

The elastomers prepared from LBH X05 and LBH X10 have the same or somewhat higher tensile strength, compression stability and hydrolytic resistance compared with the elastomer based on PolyBd R45HT. As expected, a significant difference was observed in the glass transition temperatures which were higher for Krasol-based polyurethanes.

Thermooxidative Stability of Functionalized Polybutadienes and Polyurethane Elastomers

Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were used to study the thermooxidative stability of the HTPB products (Table III). Upon heating in air atmosphere, polybutadiene and oxygen are involved in a variety of free-radical reactions. The oxidation reaction is indicated by an exothermic peak on the DSC curve. The stability of polymers to thermo-

TABLE III

Thermooxidative properties of hydroxy-terminated polybutadienes functionalized with 2-sulfanylethan-1-ol and of corresponding polyurethane elastomers

Parameter	LBH X02	LBH X05	LBH X10	LBH X20	LBH 2000 ^a	polyBd ^b	PolyBd+Irg ^c
DSC of HTPB							
T_e (°C)	221	234	252	272	189	147	176
T_{max} (°C)	257	269	285	302	226	221	225
TGA of HTPB							
T_i (°C)	176	182	185	176	180	150	202
DSC of polyurethane elastomer^d							
T_e (°C)	211	227	234	245	200	173	–
T_{max} (°C)	235	288	294	299	218	206	–

^a Krasol LBH 2000; ^b PolyBd R45HT; ^c PolyBd R45HT stabilized with 0.2 wt.% of Irganox 1520; ^d composition and properties of polyurethane elastomers are given in Table II.

oxidation can be characterized by the extrapolated peak onset temperature (T_e) and maximum peak temperature (T_{\max}).

Polybutadiene diol Krasol LBH 2000 is stabilized by Irganox 1520. The DSC measurements revealed that functionalization with 2-sulfanylethan-1-ol further improves the thermooxidative stability of the polybutadiene. The stability increases with the amount of introduced thiol. For instance, the values T_e and T_{\max} for LBH X05 and/or LBH X10 are by about 40 and/or 60 °C higher compared with the neat polybutadiene diol Krasol LBH 2000.

The thermooxidative stability of PolyBd R45HT was lower than that of Krasol LBH 2000, most probably due to the absence of any antioxidant. After addition of 0.2% of Irganox 1520 to the PolyBd product, the values of T_e and T_{\max} were closer to those of Krasol LBH 2000.

The DSC results on the thermooxidative resistance of the HTPB products were supported by TGA measurements. TGA curves showing the initial stages of the polymer degradation are given in Fig. 1. Weight increase as a result of the reaction with oxygen could be detected on all thermograms. The peak onset temperatures T_i for individual products fell into the interval from 150 to about 200 °C (cf. Table III). A slight loss of polybutadiene weight observed between about 100 and 200 °C was probably due to the release of volatiles present in the products (max. 0.3%). The subsequent drop in weight at higher temperatures can be attributed to the onset of polymer decomposition.

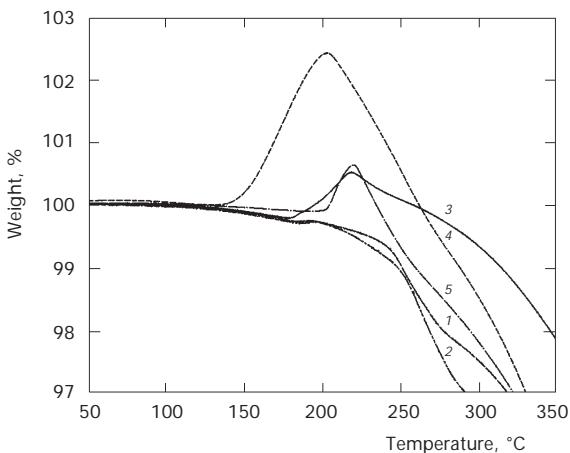


FIG. 1
TGA curves of hydroxy-terminated polybutadienes: LBH X05 (1), LBH X10 (2), Krasol LBH 2000 (3), PolyBd R45HT (4) and PolyBd R45HT stabilized with 0.2 wt.% of Irganox 1520 (5)

By far the highest extent of the oxidation reaction was observed with PolyBd R45HT. When stabilized with Irganox 1520, the polymer exhibited a much lower weight increase, similar to that of Krasol LBH 2000. TGA plots of polybutadienes functionalized with 2-sulfanylethan-1-ol differed markedly from the curve of the virgin polymer. With increasing degree of functionalization the weight changes related to the thermooxidation gradually decreased.

Thermooxidative properties of the polyurethane elastomers were studied by DSC. As mentioned before, the isocyanate component of the formulation was a commercial prepolymer Krasol NN-22, which is manufactured from the neat polybutadiene diol Krasol LBH and is stabilized by Irganox 1520. The data in Table III clearly demonstrate higher stability for the elastomers based on functionalized polymers despite the fact that these materials contained a significant portion of virgin polybutadiene. The values of T_e and T_{max} of the polyurethanes reflect the degree of HTPB functionalization.

The PolyBd-based polyurethane was less resistant to thermooxidation. The obtained value of T_e , however, appears to be affected by the antioxidant contained in Krasol NN-22.

CONCLUSIONS

Functionalization of hydroxy-terminated polybutadiene Krasol LBH 2000 was achieved by a radical addition of 2-sulfanylethan-1-ol initiated with 2,2'-azobis(isobutyronitrile). The reaction proceeds without solvent, with practically total conversion of the mercaptan, and under conditions allowing an industrial scale-up.

The functionalization not only increases the hydroxy functionality of the polybutadiene in a controlled way, but also improves its thermooxidative stability as confirmed by DSC and TGA measurements. The global characteristics of polymers such as viscosity and glass transition temperature are also affected by the addition of 2-sulfanylethan-1-ol.

The role of hydroxy functionality of polybutadienes was shown in a polyurethane elastomer system. The increasing functionality accelerates the crosslinking reaction, increases the elastomer hardness, improves compression-set characteristics and thermal stability. The elastomers based on functionalized polybutadienes exhibited higher resistance to thermooxidation.

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